First satellite observations of lower tropospheric ammonia and methanol

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[1] The Tropospheric Emission Spectrometer (TES) on the EOS Aura satellite makes global measurements of infrared radiances which are used to derive profiles of species such as O_3, CO, H_2O, HDO and CH_4 as routine standard products. In addition, TES has a variety of special modes that provide denser spatial mapping over a limited geographical area. A continuous-coverage mode (called ''transect'', about 460 km long) has now been used to detect additional molecules indicative of regional air pollution. On 10 July 2007 at about 05:37 UTC (13:24 LMST) TES conducted such a transect observation over the Beijing area in northeast China. Examination of the residual spectral radiances following the retrieval of the TES standard products revealed surprisingly strong features attributable to enhanced concentrations of ammonia (NH_3) and methanol (CH_3OH), well above the normal background levels. This is the first time that these molecules have been detected in space-based nadir viewing measurements that penetrate into the lower atmosphere. **Citation:** Beer, R., et al. (2008), First satellite observations of lower tropospheric ammonia and methanol, *Geophys. Res. Lett.*, *35*, L09801, doi:10.1029/2008GL033642.

1. Introduction

[2] This paper presents a preliminary analysis of TES space-based spectra of ammonia and methanol (methyl alcohol) acquired in the Beijing area in July 2007. Both species are regionally and locally important in tropospheric chemistry.

[3] Methanol is the most abundant oxygenated hydrocarbon gas in the atmosphere and is therefore a major contributor to non-methane volatile organic compounds (NMVOC) [*Singh et al.*, 1995]. *Jacob et al.* [2005] developed a global methanol budget, and argue that globally, plant growth is the largest source, followed by atmospheric production, plant decay, and biomass burning. In the remote troposphere, methanol concentrations are 0.1 to 1 ppb [*Singh et al.*, 1995] while the concentrations in the continental boundary layer are an order of magnitude larger. Measurements in Innsbruck, Austria [*Holzinger et al.*, 2001] show a peak in June, consistent with plant growth being the dominant source. Methanol concentrations in the 4.6 to 13 ppb range have been reported near Barcelona [*Filella and Peñuelas*, 2006] with a maximum in June, but no specific source was identified, as the sampling was near anthropogenic and biogenic sources.

[4] Boundary layer ammonia concentrations vary widely, and as ammonia is readily absorbed by surfaces, it has a rather short atmospheric lifetime, on the order of a few hours [*Dentener and Crutzen*, 1994]. The most significant sources are animal waste, soil, fertilizers, and industrial emissions, and elevated concentrations are generally correlated with nearby industrial or agricultural regions [*Fangmeier et al.*, 1994]. *Streets et al.* [2003] provided a detailed inventory of gaseous and primary aerosol emissions in Asia, and report that fertilizer application and animals account for 83% of ammonia emissions. *Yamaji et al.* [2004] provide a detailed region specific emission inventory from animal farming in Asia, and in that work they find that the highest ammonia emissions per area are found along the lower part of the Yellow River and the North China Plain. European measurements report concentrations on the order of 1 ppb [*Galperin and Sofiev*, 1998; *Burkhardt et al.*, 1998]. In a study near Rome, Italy, background concentrations also near 1 ppb were observed, but urban traffic station measurements were an order of magnitude larger [*Perrino et al.*, 2002]. Measurements near Tampa, Florida showed background concentrations of 1.4 ppb, and mean concentrations of 3.5 ppb for measurements impacted by local sources [*Myles et al.*, 2006]. Ammonia can play an important role in secondary aerosol formation when gas phase sulfate or nitrate are present.

[5] Both species have been detected in the upper troposphere by limb sounders (ACE, MIPAS) [*Dufour et al.*, 2006, 2007; *Coheur et al.*, 2007; *Burgess et al.*, 2006]. Thus the capability to measure ammonia and methanol from space will greatly add to the currently sparse knowledge of atmospheric concentrations and annual variability of these species, contributing to our understanding of global and regional atmospheric chemistry.

2. Observations

[6] On July 10 2007 between 05:34:52 & 05:39:14 UTC (13:23–13:24 LMST) TES conducted a transect observation over northeast China between latitudes +37.988 & +41.998, east longitudes 117.014 & 115.746 (a distance of some 460 km) in the Beijing area. The individual observations (40 in all) require 4 seconds each with ~1.5 seconds reset time in between. The ground track runs slightly to the northwest, beginning in the plain south of Beijing near the coast and ending in the highlands to the north.

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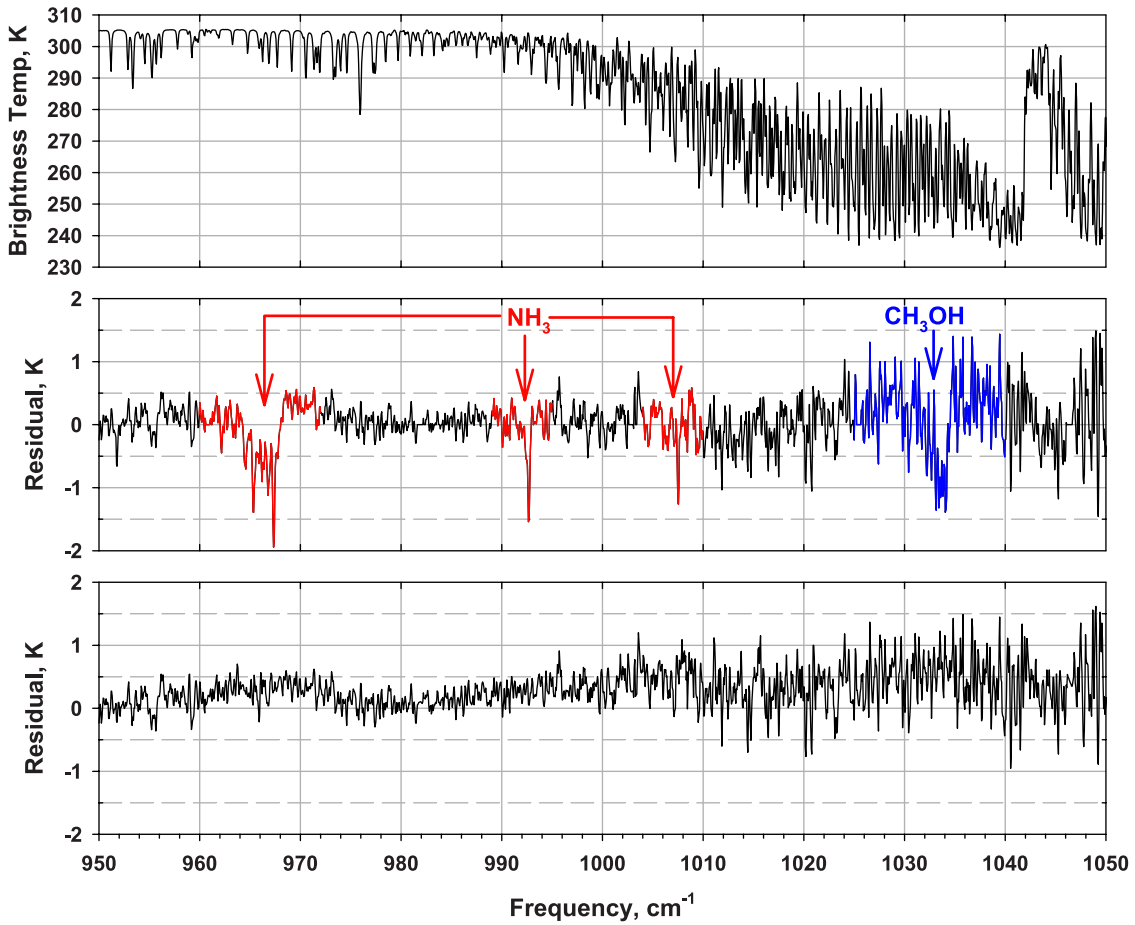

Figure 1. (top) Portion of a spectrum acquired south of Beijing plotted on a brightness temperature scale. The major features are due to CO_2 (950–990 cm^{-1}) and O_3 (990–1050 cm^{-1}). (middle) Residual spectrum (Observed – Calculated) after accounting for the major species. The red-highlighted signatures are from NH_3 and those in blue indicate CH_3OH. (bottom) Residual spectrum after both NH_3 and CH_3OH have been added to the calculated forward model.

[7] In order to provide a reasonable comparison, we have also analyzed a similar transect over an area near San Diego, CA one month earlier. It was chosen because the surface temperatures and terrain (low in the south, hilly in the north) are similar to the Beijing area.

3. Residual Analysis

[8] Standard (routine) quantitative analysis follows well-known principles [e.g., *Rodgers*, 2000]: based on an initial guess about the atmospheric state (species and temperature profiles) a forward spectral radiance model is constructed and compared to the observed radiance. Using appropriate constraints (because the problem is both ill-posed and mostly non-linear), the forward model is iterated until the difference [observed – calculated] is minimized. If all species have been properly accounted for, the difference should reflect only the measurement noise. Spectral differences between the observed and calculated radiances are termed spectral residuals and may be due to unexpected species in the atmosphere. Such is the case here where quite marked (and identifiable) spectral residuals are evident.

[9] Although the residuals are prominent (Figure 1), they are spectroscopically weak (~1% of the continuum level even at the TES spectral resolution of 0.06 cm^{-1}). Given that, the individual lines fall in the regime where their strength is proportional to the column density. Hence it follows directly that the retrieval will also be linear and all that is required is a reasonable initial guess profile and the Jacobians (calculated simultaneously with the forward radiance model, themselves based on HITRAN2004 [*Rothman et al.*, 2005] *via* LBLRTM11.2 [*Clough et al.*, 2005]). However, it also follows that there can be no more than about 1 degree of freedom for signal.

[10] The abundances of ammonia and methanol are estimated from the spectral residual differences in the 960–972 cm^{-1} and 1026–1040 cm^{-1} regions, respectively, between TES measured radiances and the TES forward model radiances [*Clough et al.*, 2006] where the effects of pressure, temperature, water vapor, ozone, surface temperature, and emissivity have been removed by the TES operational retrieval algorithm [*Bowman et al.*, 2006]. Profile scaling factors are through a constrained linear process that minimizes the remaining spectral residuals. The scaling factors are applied directly to the ammonia

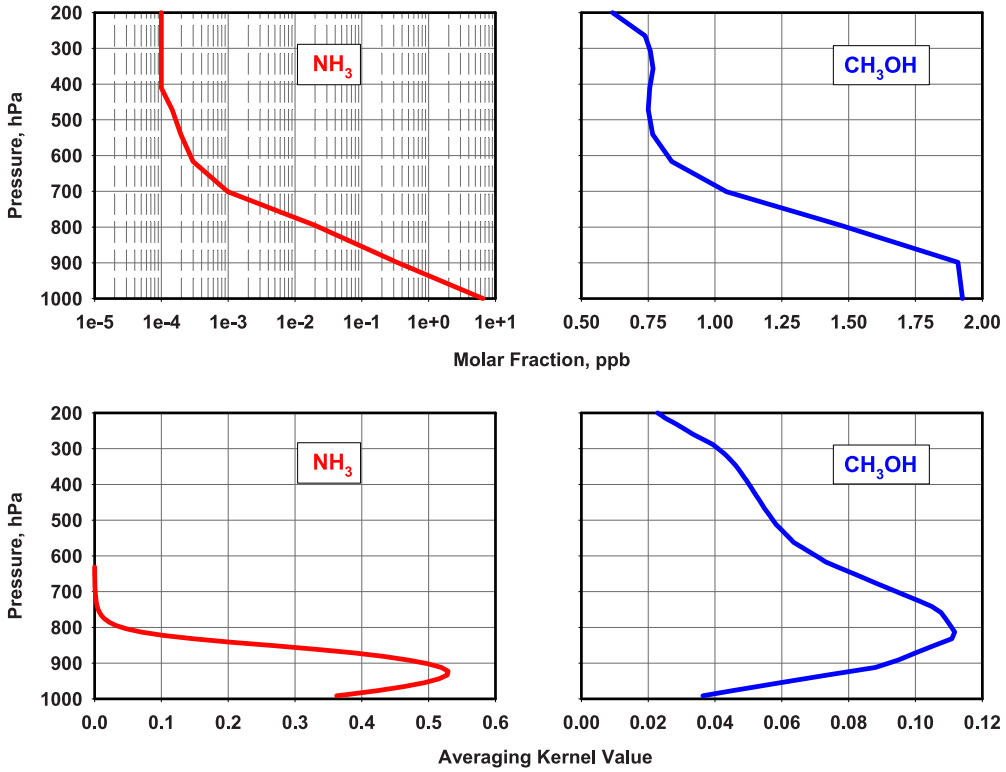

Figure 2. (top row) Assumed initial guess profiles for NH_3 and CH_3OH. (bottom row) Representative averaging kernels for these profiles.

and methanol profiles shown in Figure 2. The initial guess ammonia profile was derived from ground based FTIR observations in Australia [*Paton-Walsh et al.*, 2005; G. Guerova, University of Wollongong, personal communication, 2007] and the methanol profile is a mean continental profile from the GEOS-CHEM Chemical Transport Model (CTM) (D. B. Millet et al., New constraints on terrestrial and oceanic sources of atmospheric methanol, submitted to *Atmospheric Chemistry and Physics*, 2008). In addition to the scaling factors, a smooth background radiance term was also estimated to account for residual systematic errors in the selected spectral regions.

[11] The same approach was also used to estimate NH_3 and CH_3OH loading near San Diego, CA acquired 1 month earlier, which has similar surface temperatures and topography. The retrieved abundances are significantly smaller and more representative of "background" conditions.

[12] The results are presented as averaging kernel weighted molar fraction (AKWMF) which is the weighted average of the scaled profile with the averaging kernel (Figure 2) as the weighting function. The approach is related to that described by V. H. Payne et al. (Information-centered representation of retrievals with limited degrees of freedom for signal: Application to methane from the Tropospheric Emission Spectrometer, submitted to *Journal of Geophysical Research*, 2008). This has the advantage that it automatically accounts for the pressure regime being sensed by the measurements and variations in terrain height and satellite viewing angle. The AKWMF of the unscaled vertical profiles shown in Figure 2 are 3.91 ppb for ammonia and 0.97 ppb for methanol. Examination of the averaging kernels shows that TES retrievals are primarily sensitive in the 850–990 hPa range for ammonia and 300–950 hPa for methanol. Note that were the true ammonia profile flatter (i.e., more like methanol) the averaging kernel peak would be at a lower pressure.

4. Results and Discussion

[13] The methanol and ammonia AKWMFs that were retrieved from the TES measurements over China and over similar conditions in North America are shown on maps in Figure 3. Over China, the values for methanol range from 3 to 5 ppb, and from 1.5 to 3.5 ppb over North America. Ammonia concentrations over China range from 5 to almost 25 ppb, while over North America they are consistently less than 5 ppb. In Figure 4, the spatial variations over China can be seen with error bars, highlighting the variability of ammonia relative to methanol.

[14] Relative to concentrations reported in the literature, the methanol observed over China is consistent with levels seen in urban areas (Innsbruck, Austria and Barcelona, Spain). Ammonia concentrations are similar to reported atmospheric concentrations near local sources. From Figure 4, it is clear that these two species are not highly correlated, but given that they have different primary sources (plant growth for methanol, livestock and fertilizer for ammonia), this is to be expected.

[15] We also note that that these two pollutants were accompanied by high concentrations of both CO and O3 (up to 200 ppb; K. W. Bowman et al., Ozone and CO over Beijing, China during the summer/fall 2007 from the

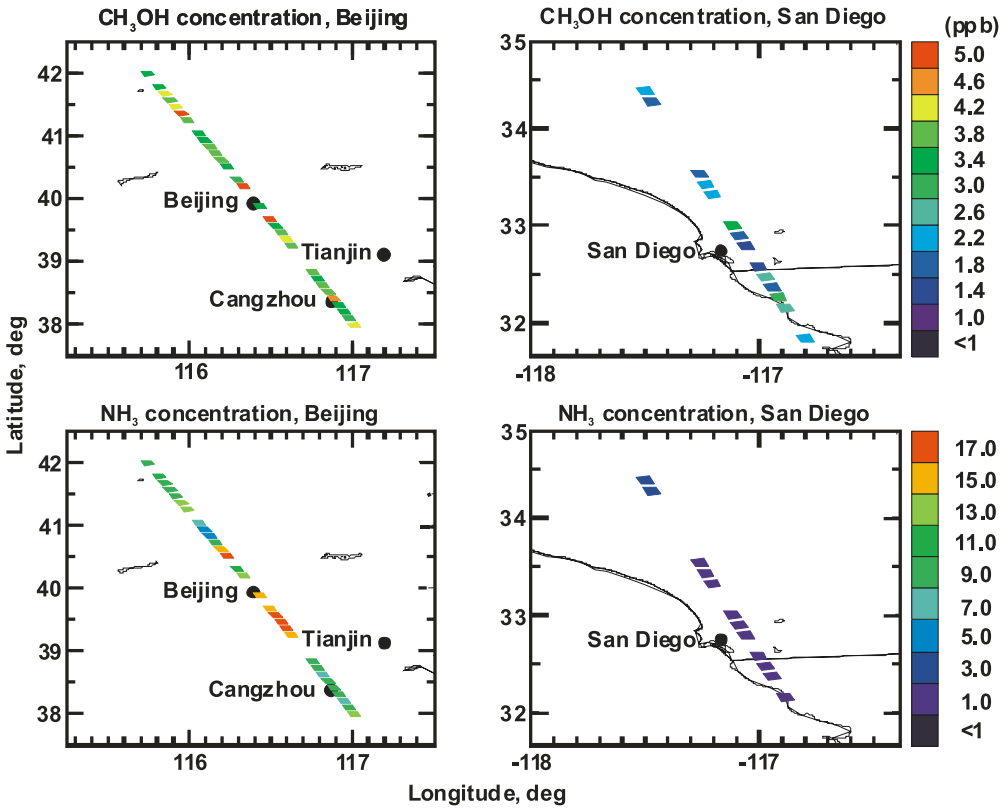

Figure 3. (top left) Retrieved CH_3OH Averaging Kernel Weighted Molar Fractions (AKWMF) in the Beijing area (see text for explanation). (top right) For comparison, retrieved CH_3OH values near San Diego, CA, area one month earlier. (bottom left and right) AKWMF for NH_3 acquired simultaneously with the CH_3OH. Parallelepipeds are roughly the projected size of the TES footprint. Gaps in the ground tracks are due to clouds.

Tropospheric Emission Spectrometer (TES), manuscript in preparation, 2008). *Jacob et al.* [2005] and *Fu et al.* [2007] show that in this area and season the burning of crop residues is common. We therefore conjecture that the sources are local rather than transported from elsewhere.

5. Future Plans

[16] This paper reports the first detection of methanol and ammonia from nadir viewing remote sensing instruments, demonstrating the possibility of characterizing these species, especially in regions of elevated concentrations. The next step is to extend the analysis potentially to provide global detection of these species. Very little is known about regional and temporal variations of concentrations, yet methanol is an important chemical in the global budget of tropospheric ozone, and ammonia deposition can be an

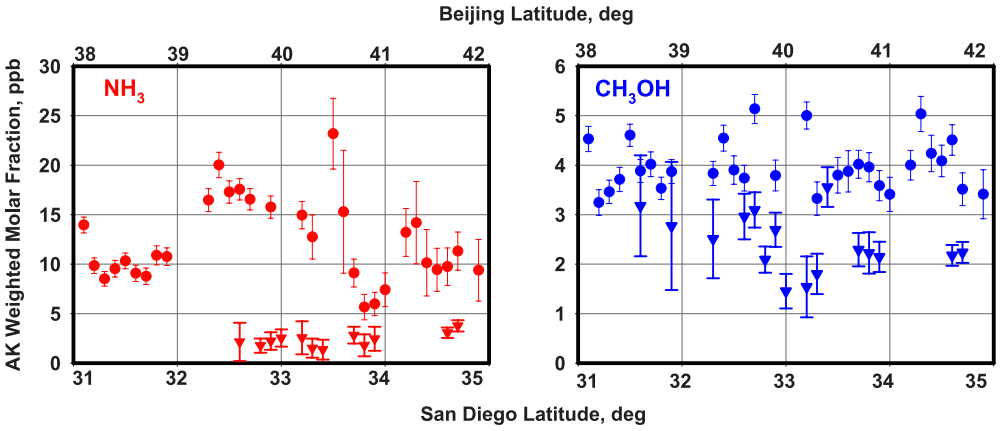

Figure 4. Along-track AKWMF for (left panel) NH_3 and (right panel) CH_3OH for the Beijing area (filled circles) and the San Diego area (filled triangles). The error bars are 2 sigma of the measurement error to provide an allowance for other unassessed errors.

important contributor to nitrogen deposition and aerosol formation in some regions.

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